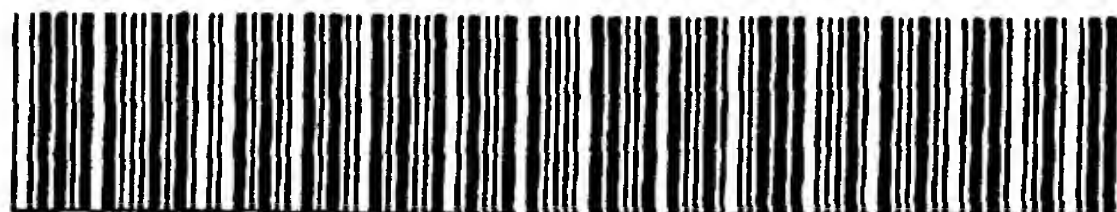


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<b>(21) International Application Number:</b> PCT/US95/09907 <b>(22) International Filing Date:</b> 4 August 1995 (04.08.95)  <b>(30) Priority Data:</b> 08/294,163                      22 August 1994 (22.08.94)                      US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).  <b>(72) Inventors:</b> NOVAK, Leo, R.; 209 Arrowwood Road, Lake Jackson, TX 77566 (US). MILLER, Robert, C.; 5220 Hedgewood Drive No. 908, Midland, MI 48640 (US). NICHOLS, Kevin, L.; 305 Rosemary Lane, Lake Jackson, TX 77566 (US).  <b>(74) Agent:</b> MORSE, Jonathan, W.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> FILLED CARBONATE POLYMER BLEND COMPOSITIONS HAVING IMPROVED IMPACT RESISTANCE  <b>(57) Abstract</b>  Filled blends of (A) carbonate polymers and (B) monovinylidene aromatic copolymers are prepared having improved combinations of resistance to linear thermal expansion and low temperature toughness. A wax additive (C) is employed which improves the low temperature toughness of the filled polymer blend. The wax additive is preferably ester wax, acid wax, polyethylene wax, or a blend of two or more of these waxes, with ester wax being the preferred wax. Preferably, specifically shaped, small particle size fillers (D) are employed which provide the resistance to linear thermal expansion and maintain the impact resistance of the filled blend. Optionally, the blend also comprises a rubber impact modifier (E) to provide improved toughness in molded articles prepared from the filled blend. These components are employed generally in amounts of from 50 to 95 percent by weight (A) and from 5 to 50 percent by weight (B) based on weight of components (A), (B) and (E); from 0.1 to 5 percent by weight (C) and from 1 to 17 percent by weight (D) based on weight of components (A, B, C, D and E); and optionally from 1 to 20 percent by weight (E) based on weight of components (A), (B) and (E).		

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# FILLED CARBONATE POLYMER BLEND COMPOSITIONS HAVING IMPROVED IMPACT RESISTANCE

The present invention relates to filled polymer blend compositions comprising a carbonate polymer, a monovinylidene aromatic copolymer and an inorganic filler. It has  
5 unexpectedly been found that certain waxy additives provide these blends with improved impact resistance, particularly at lower temperatures. More particularly, the present invention relates to such a blend having improved combinations of linear thermal expansion, impact resistance, modulus (stiffness), melt flow (melt processability) and heat resistance. These compositions are particularly useful in the preparation of molded objects, particularly parts  
10 having large surfaces prepared by injection molding techniques and requiring predictable finished dimensions and smooth, surface finishes. Such properties are particularly desired for exterior automotive body panels.

The utilization of carbonate polymer blends in a number of applications has typically been limited due to the fact that these polymers have a relatively high coefficient of  
15 linear thermal expansion (CLTE). The CLTE value reflects the tendency of a material to undergo dimensional changes due to thermal fluctuations, especially when in the form of larger molded or extruded articles. For example, if a door or fender component of an automobile expands or contracts excessively in extremely hot or cold conditions it would normally result in buckling or misfit in the assembled finished product and/or stress fracturing at the point of fastening.  
20 Otherwise, there must be sufficient compensation in the product construction or fastening device for the expansion and contraction of the sheet or part.

In applications such as exterior automotive parts, it is also essential to provide low temperature impact resistance. While it is possible to provide improved coefficients of linear thermal expansion in carbonate polymer blends by the incorporation of increased amount of  
25 fillers, impact resistance, particularly low temperature impact resistance, is often reduced to unacceptable levels by fibrous fillers. Moreover, fibrous reinforcing additives such as glass fiber are very efficient in lowering the CLTE in the flow direction but not in the cross flow direction and typically produce unacceptable surface properties that are visible on the surface of the resulting molded objects.

30 In the past, various techniques have been employed in attempting to prepare or modify filled carbonate polymer blends to reduce or eliminate these limitations.

In JP 52-63,954 (1977) there are disclosed blends composed of 20 to 45 weight percent of an ABS resin, 45 to 20 weight percent of a polycarbonate resin and from 5 to 30 weight percent talc. In JP 138,550 (1987) polybutylene terephthalate is added to  
35 polycarbonate/inorganic filler blends to attempt to improve toughness. In U.S. Patent 5,091,461, it is shown that specified talc fillers, having the proper small size and plate shape provide specific blends of carbonate and rubber modified vinyl aromatic polymers with good combinations of CLTE, toughness and resistance to heat distortion.

In EP 135,904 it is shown that specified blends of poly(ethylene terephthalate), carbonate polymer and grafted rubber impact modifiers have good combinations of impact strength and resistance to warpage when containing talc filler. U.S. Patent 4,098,734 discloses blends comprising a matrix interpolymer, a grafted rubber copolymer, a polymer other than  
5 the two foregoing polymers having a solubility parameter in the range of 8.5 to 13 and an inorganic filler. U.S. Patent 4,763,133 discloses, as a layer in multilayer laminate antenna structure, blends of certain thermoplastic resins with inorganic fillers, including glass fiber, talc or clay. The filler is added to lower the coefficient of linear thermal expansion while raising the flexural modulus. Carbonate polymer is listed among the numerous thermoplastic resins  
10 alleged to be suitable for use in this layer of the laminate.

U.S. Patent 3,424,703 discloses that from 0.025 to 0.5 weight percent silica or talc fillers with a particle size up to 10 micrometers can be incorporated into aromatic polycarbonates to provide thin, relatively haze-free films with a low coefficient of linear thermal expansion.

15 In view of the continuing need for improved combinations of properties in engineering thermoplastics, it would be desirable if there were provided a filled polymeric blend with improved combinations of physical properties including CLTE, impact resistance (especially at low temperatures) and resistance to heat distortion.

According to the present invention there is now provided polymer blend  
20 compositions comprising (A) carbonate polymer; (B) monovinylidene aromatic copolymer; (C) a wax which improves the low temperature toughness of the blend; (D) an inorganic filler; and optionally, (E) a rubber impact modifier.

In a specific preferred embodiment, the present invention is a filled polymer blend composition comprising (A) carbonate polymer in an amount of from 50 to 95 percent by  
25 weight based on weight of components (A), (B) and (E); (B) monovinylidene aromatic copolymer in an amount of from 5 to 50 percent by weight based on weight of components (A) and (B) and (E); (C) a wax in an amount of from 0.1 to 5 percent by weight based on weight of components (A), (B), (C), (D) and (E), which wax improves the low temperature toughness of the filled blend; (D) an inorganic filler in an amount of from 1 to 17 percent by weight based on  
30 weight of components (A), (B), (C), (D) and (E), which inorganic filler preferably has an average diameter to thickness ratio (D/T) of from 4 to 24; and optionally, (E) a homopolymer or copolymer of butadiene in amounts up to 20 percent by weight based on weight of components (A) and (B) and (E).

In a further aspect, the present invention is also an improved, large molded article  
35 having a surface area greater than 400 square inches, which article is prepared from a polymer blend according to the invention described above. Preferably the article has a smooth surface and a coefficient of linear thermal expansion (CLTE) per ASTM D-696 equal to or less than  $3.7 \times 10^{-5}/^{\circ}\text{F}$  ( $6.7 \times 10^{-5}/^{\circ}\text{C}$ ). More preferably an article prepared from the blend will have a dart

impact strength at -20°F (-29°C) per ASTM D-3029 of at least 200 inch pounds (in/lbs) (22.6 joules), a heat distortion temperature under load (DTUL) per ASTM D-648-82 at 66 psi (455 kPa) of at least 240°F (116°C), and a flexural modulus of at least 350,000 pounds per square inch (psi) (2400 MPa). In another aspect, the present invention is a molded automotive exterior body panel prepared from a polymer blend according to the invention described above.

A key aspect in the preparation of the improved blends according to the present invention is the use of an appropriate wax additive. While the theory is not completely understood, it is believed that certain wax additives have a desirable interaction with the filler particles and facilitate their dispersion and incorporation into the blend of carbonate and monovinylidene aromatic polymers. The most noticeable effect of the wax is the unexpected improvement in the low temperature toughness of articles molded from the blends while maintaining a desirably low coefficient of linear thermal expansion and good resistance to heat distortion under load. It was also found that the wax additive unexpectedly resulted in less notch sensitivity in the room temperature impact resistance. In view of the simultaneous improvement in the processability of the resins according to the present invention, benefits can also be obtained when the resins according to the present invention are employed in the molding of large parts, for example having a surface area of at least 400 square inches (dimensions of at least 20 inches by 20 inches), having a smooth surface and excellent appearance.

Thus, the preferred waxes for use according to the present invention are those which result in an improvement in the low temperature toughness of a filled carbonate/monovinylidene aromatic polymer blend as measured by the Dart Impact Resistance test method (at -20°F) by at least 20 percent as compared to the blend not containing the wax while the CLTE of the blend is maintained within 10 percent of the CLTE measured without the wax when the filled blend contains 14 weight percent of the filler and 2 weight percent of the wax.

Waxes suitable for use according to this invention are known organic compounds or mixtures of such compounds which are solids at room temperature but which have a relatively low melting point as compared to most thermoplastic molding resins. There are both natural and synthetic waxes. Some are hydrocarbons, others are esters of fatty acids and alcohols. With regard to the waxes suitable for use according to this invention, it is noted that a non-basic wax is desired since basic waxes, such as the known amide-containing (bis)stearamide waxes, exhibit reactivity with the carbonate polymer and cause degradation of the carbonate polymer molecular weight. In general, it has been found that suitable waxes include and can be selected from the group consisting of the ester waxes and acid waxes; preferably the Montan derivative ester waxes and the acid waxes; the polyethylene (PE) waxes, both polar and non-polar; and mixtures of two or more of these waxes. Especially preferred are the Montan ester waxes and the polyethylene waxes. Avoiding the amide-containing



(bis)stearamide waxes is essential to optimized properties of the resin blend compositions. In general, depending upon the specific wax type, the suitable waxes have molecular weights of at least 100, preferably at least 200 and more preferably at least 400. Again, depending upon the specific wax type, the main types of suitable waxes (montan ester and acid waxes) generally have molecular weights up to 5,000, preferably up to 2,000, more preferably up to 1,000. For the polyethylene-type waxes, however, the typical molecular weights are generally up to 10,000, preferably up to 9,000.

The ester-type waxes, and in particular the Montan ester-type waxes, are known in the literature and are produced by the esterification of Montanic acid or extraction from lignite. Montanic ester-type waxes are commercially available products such as, for example, Hoechst-Wachs E, commercially available from Hoechst-Celanese. These waxes preferably have a molecular weight in the range of 500 to 1000. These waxes typically have an acid number of at least 6, preferably at least 10 and most preferably at least 15, the acid number units being milligrams KOH required to neutralize one gram wax (mg KOH/g) by titration. Desirably, the acid number is less than or equal to 30, preferably 25 and most preferably 20 mg KOH/g wax. The ester waxes also are characterized by their saponification number, with saponification numbers for desirable ester waxes being at least 80, preferably at least 100, most preferably at least 130 and typically not more than 200, preferably not more than 180 and more preferably not more than 160.

The polyethylene waxes are known in the literature and are commercially available, for example from Hoechst in various grades identified under the tradename Hoechst-Wachs PE 190 and PED 191. The polyethylene waxes are produced by polymerization or oligomerization of olefin monomer or monomer mixture up to molecular weights of 10,000, preferably up to 9,000. Polar versions are available and have acid values in the range of 10 to 70, preferably 10 to 30 mg KOH/g and saponification values in the range of 10 to 120, preferably 15 to 70 and more preferably 15 to 50. Non-polar polyethylene waxes are commercially available products such as, Hoechst Wachs PE 190 while polar polyethylene waxes are commercially available as Hoechst Wachs PED 191, both from Hoechst-Celanese.

The Montan acid-type waxes are known in the literature and are commercially available, for example, from Hoechst-Celanese as Hoechst Wachs S. These waxes are typically obtained by extraction from lignite. These waxes preferably have a molecular weight in the range of from 400 to 700, and an acid number of at least 100, preferably at least 130 and less than or equal to 180, preferably less than or equal to 150.

The suitable wax (including a mixture of waxes), is generally added in amounts that provide the desired improvement in the low temperature toughness of the blend. Usually, the wax is added in amounts of at least 0.1 weight percent wax, based on weights of wax, filler, carbonate and monovinylidene aromatic polymers, and optional impact modifier, more preferably at least 0.5, and most preferably at least 1 weight percent. Usually it has been found

sufficient to employ less than or equal to 5 weight percent wax, based on weights of wax, filler, carbonate and monovinylidene aromatic polymers and optional impact modifier, more preferably less than or equal to 4 weight percent, and most preferably less than or equal to 3 weight percent.

5           The carbonate polymer resins usefully employed according to the present invention are those previously known and described in the prior art. As known, such resins include the carbonate resins obtained by the interfacial, melt or solution polymerization of a dihydroxy monomer compound, preferably a dihydroxyaryl compound, especially a bis-dihydroxyarylalkane with a polycarbonate precursor such as phosgene, a bischloroformate or a  
10       dicarbonate such as diphenyl carbonate or dimethyl carbonate. Preferably the carbonate polymer is an aromatic carbonate polymer, more preferably it is prepared from an aromatic diol such as bisphenol A, tetrabromo-bisphenol A, tetramethyl bisphenol A, 1,1-bis(4-hydroxyphenyl)-1phenylethane, bishydroxyphenylfluorene or mixtures of two or more of these.

15           In addition to the suitable polycarbonates prepared by exclusive use of one or more of the above diols, carbonate polymers suitable for use according to the claimed invention could be prepared in the presence of an amount of a diacid or diacid chloride to produce the known poly(ester-carbonates).

          These carbonate polymers are employed in the blends according to the invention  
20       in amounts sufficient to provide the desired levels of toughness and resistance to heat. In general the carbonate polymer is employed in an amount of at least 50, preferably at least 55 and more preferably at least 60 percent by weight based on weight of carbonate and monovinylidene aromatic polymers. Usually the carbonate polymer is employed in an amount of up to and including 95, preferably up to and including 90 and more preferably up to and  
25       including 70 percent by weight based on weight carbonate and monovinylidene aromatic polymers.

          The carbonate polymers suitable for use in the present invention include a broad range of the known carbonate polymers in terms of molecular weight or melt flow rate (which is an indirect indication of resin molecular weight). In general, to obtain the desired  
30       processability, the carbonate polymer molecular weight should provide a resin melt flow rate (MFR) of at least 3 grams per 10 minutes (as measured by ASTM 1238-35, condition O), preferably at least 3.5, more preferably at least 5, more preferably at least 7, and most preferably at least 10. In order to provide the desired level of physical properties, including toughness, the carbonate polymer molecular weight should be high enough to provide a resin  
35       melt flow rate (MFR) of less than or equal to 80 grams per 10 minutes, preferably 40, more preferably 20, and most preferably 12.

          The monovinylidene aromatic copolymers suitably employed according to the present invention include copolymers of one or more monovinylidene aromatic monomer, such

as styrene, alpha methyl styrene and/or ring substituted styrenes, with one or more additional unsaturated, copolymerizable monomers, particularly the ethylenically unsaturated nitrile monomers (such as acrylonitrile, methacrylonitrile and/or fumaronitrile), maleic acid derivatives such as maleic anhydride, alkyl (meth)acrylates such as methylmethacrylate, N-substituted maleimides such as N-phenylmaleimide or other polymerizable comonomers.

Such monovinylidene aromatic copolymers typically contain at least 40, preferably at least 50, more preferably at least 70 weight percent monovinylidene aromatic monomer and up to 90 preferably up to 85, weight percent monovinylidene aromatic monomer based on weight monovinylidene aromatic copolymer. Highly preferred copolymers contain from 70 to 85 percent styrene monomer and 15 to 30 percent acrylonitrile monomer. The suitable monovinylidene aromatic monomers include the lower alkyl-substituted (from 1 to 4 carbon atoms) and halogen-substituted styrenes, where the substitution can be on the aromatic ring or the vinyl moiety. Monovinylidene aromatic copolymers with one or more additional unsaturated, copolymerizable monomer are preferred versus homopolymers of the monovinylidene aromatic monomers due to their better compatibility with the carbonate polymer.

In general, the monovinylidene aromatic copolymer is employed in amounts to improve the processability of the blend composition and maintain the desired physical properties. The monovinylidene aromatic copolymer is typically incorporated into the blend of the present invention in amounts of at least 5 weight percent, preferably at least 10 weight percent and more preferably at least 25 weight percent, said weight percentage being based on weight of carbonate polymer and monovinylidene aromatic copolymer components. In order to maintain the resin blend physical properties the monovinylidene aromatic copolymer is typically incorporated into the blend of the present invention in amounts of less than or equal to 50 weight percent, preferably less than or equal to 45 weight percent, and most preferably less than or equal to 40 weight percent based on total weight of the carbonate polymer and monovinylidene aromatic copolymer components.

The various types of optional rubber impact modifier materials suitable for use in compositions according to the invention can be incorporated in several different fashions. The optional rubber materials are commonly incorporated in the blends according to the invention in order to improve the toughness and impact resistance. Grafting or other compatibilization techniques are desirably used to improve compatibility and miscibility with the carbonate and/or monovinylidene aromatic polymer components. As is known a rubber-modified monovinylidene aromatic copolymer can be prepared and used to provide both the monovinylidene aromatic copolymer and rubber components. As is also well known, a separately prepared grafted impact modifier having a higher rubber content and little or no free or ungrafted polymer can be incorporated as a separate component.



In general, the optional rubber materials have elastic properties and have glass transition temperatures ( $T_g$ 's) less than  $0^\circ\text{C}$ , generally less than  $-10^\circ\text{C}$ , preferably less than  $-20^\circ\text{C}$  and more preferably less than  $-30^\circ\text{C}$ . Suitable rubbers include the well known homopolymers and copolymers of conjugated dienes, particularly butadiene; as well as other rubbery polymers such as olefin polymers, particularly copolymers of ethylene, propylene and optionally a nonconjugated diene. In addition, mixtures of the foregoing rubbery polymers may be employed if desired. Preferred rubbers are homopolymers of butadiene and copolymers thereof with up to 30 percent by weight styrene. Such copolymers may be random or block copolymers and in addition may be hydrogenated to remove residual unsaturation.

Where incorporated, the rubbers are optionally grafted with an amount of a graft polymer, such as a monovinylidene aromatic copolymer, including polymers of styrene and either acrylonitrile or methyl methacrylate, that compatibilizes the rubber component with the carbonate and/or monovinylidene aromatic polymers. Such graft copolymers are prepared by a graft generating process such as by a bulk or solution polymerization or an emulsion polymerization of the graft polymer in the presence of the rubbery polymer. In the emulsion polymerization to form graft copolymers of rubbery substrates it is previously known in the art to employ complete or partial agglomeration technology to prepare large rubber particles containing the copolymer grafted thereto.

An especially preferred rubber-modified monovinylidene aromatic copolymer employs a butadiene polymer rubber to modify a monovinylidene aromatic copolymer with an ethylenically unsaturated nitrile monomer such as acrylonitrile and other optional comonomer(s) such as methylmethacrylate, methacrylonitrile, fumaronitrile and/or an N-aryl-maleimide such as N-phenylmaleimide. Such copolymers are herein collectively referred to as ABS-type resins. ABS-type resins typically have a glass transition temperature ( $T_g$ ) of greater than  $0^\circ\text{C}$ , generally greater than  $20^\circ\text{C}$ , preferably greater than  $60^\circ\text{C}$ , which  $T_g$  is dictated by the matrix phase polymer.

Generally, ABS-type resins typically comprise at least 3 percent by weight rubber, preferably at least 5 percent by weight rubber, more preferably at least 8 percent by weight rubber, most preferably at least 10 percent by weight rubber, based on the weight of rubber modified monovinylidene aromatic copolymers and not including the weight of the grafted or occluded compatibilizing monovinylidene aromatic copolymer in the rubber weight. With regard to upper levels of rubber, the ABS-type rubber modified monovinylidene aromatic copolymers can comprise up to 50 percent by weight rubber, preferably up to 40 percent by weight rubber, more preferably up to 25 percent by weight rubber and most preferably up to 20 percent by weight rubber. In such ABS-type resins, the monovinylidene aromatic copolymers are prepared simultaneously with the grafting of the rubber component to prepare the optional grafted rubber impact modifier.

Preferred ABS-type rubber modified monovinylidene aromatic copolymer resins are those prepared by the solution or bulk polymerization of styrene and acrylonitrile comonomers in the presence of butadiene polymer rubber and an optional solvent or diluent. Alternatively such ABS resins may be prepared by mixing together previously prepared components comprising the monovinylidene aromatic copolymer and grafted rubbery polymer.

Other suitable monovinylidene aromatic copolymer grafted rubber components include the rubber modified polymers of styrene or  $\alpha$ -methylstyrene with other polymerizable monomers including methylmethacrylate, methacrylonitrile, fumaronitrile and/or an N-aryl-maleimide such as N-phenylmaleimide. Some of the preferred rubber-containing materials of this type are the known MBS-type core/shell grafted copolymers having a Tg less than 0°C and a rubber content greater than 40 percent, preferably greater than 50 percent. They are generally obtained by graft polymerizing styrene and methylmethacrylate and/or equivalent monomers (producing a small amount of a mostly grafted monovinylidene aromatic polymer component) in the presence of a conjugated diene polymer rubber core, preferably a butadiene homo- or co-polymer. The grafting monomers may be added to the reaction mixture simultaneously or in sequence, and, when added in sequence, layers, shells or wart-like appendages can be built up around the substrate latex, or core. The monomers can be added in various ratios to each other.

In general, it has been found desirable if employing an optional rubber component to use the optional grafted rubber in amounts to provide at least 0.5 percent by weight rubber based on weight monovinylidene aromatic, carbonate and rubber polymer components, preferably at least 1 percent and more preferably at least 2 percent. It has correspondingly been found desirable to maintain levels of the optional rubber less than or equal to 20 weight percent rubber, preferably less than or equal to 15, more preferably less than or equal to 10 weight percent based on weight monovinylidene aromatic, carbonate and rubber polymer components.

In general, the blends according to the present invention can incorporate talc, clay or a similar type of filler which provides the desired levels of physical and other property requirements such as toughness, modulus (stiffness) and resistance to linear thermal expansion. Several varieties of talc and clay filler materials have been found to be especially suitable.

As disclosed in U.S. Patent 5,091,461, elongated or plate-shaped fillers having the specified small particles have been found to better maintain the toughness properties of resin blends as compared to fibrillar or spherical shaped fillers. The relevant portions of U.S. Patent 5,091,461 relating to the disclosed talc fillers are hereby incorporated by reference herein. The suitability of the filler in maintaining the preferred levels of impact resistance of molded articles prepared from the resin has been found to be a function of the average diameter/thickness ratio (D/T) of the filler particles together with obtaining a uniformly small

particle-sized filler. Highly preferred are those compositions incorporating fillers having an average diameter/thickness ratio (D/T) as measured according to the below-described technique of at least 4, preferably at least 6, more preferably at least 7. With regard to the maximum level for the D/T ratio, it has been found desirable to have a value up to and including 30, preferably up to and including 24, preferably up to and including 18, more preferably up to and including 13, and most preferably up to and including 10.

For determining the D/T ratio, the diameter (or longest dimension) of the fillers as well as their thickness (shortest dimension of the 2 dimensions measurable) can be measured by preparing a filler modified polymeric resin sample and measuring the particle dimensions of the dispersed particles on electron photomicrographs of thin sections of the polymers. The electron photomicrograph should have a magnification of from 3000X to 15000X, preferably 7500X. By physically measuring the diameter/thickness of a representative sample of at least 25 and preferably at least 50 filler particles, one can obtain a relatively accurate value for the diameter/thickness ratio.

The inorganic fillers preferably employed according to the present invention are the known mineral talcs and clays. Preferred are the uncalcined talcs and clays having very low free metal oxide content. Talcs and clays are generally known fillers for various polymeric resins. See for example U.S. Patents 5,091,461 and 3,424,703 and EP 391,413, where these materials and their suitability as filler for polymeric resins are generally described.

The mineral talcs best suited are hydrated magnesium silicates as generally represented by the theoretical formula:



Compositions of talcs may vary somewhat with locality in which they are mined. Montana talcs, for example, closely approach this theoretical composition. Suitable mineral talcs of this type are commercially available as Microtalc MP 25-38 and Microtalc MP 10-52 from Pfizer.

The clays best suited for use are hydrous alumino silicate-type compounds, generally represented by the formula:



Suitable clay materials are commercially available as Tex 10R brand clay from Anglo American Clay Co.

As is disclosed in U.S. Patent 5,091,461, elongated or plate-shaped fillers having the specified uniformly small particles have been found to better maintain the toughness properties of resin blends as compared to fillers which are spherical shaped and/or have larger particles. To similarly obtain the most preferred polymeric blends according to the present invention it is desirable to employ specific fillers where the particles have a very small average particle size and have a relatively narrow particle size distribution. As used herein, the "average particle size" and "maximum particle size" are measured by Coulter Counter techniques. As known to those skilled in the art, Coulter Counter techniques measure these

values based on volume and give an equivalent spherical volume diameter meaning that the diameter readings are diameters that would be observed for spheres having the same volume as the plate shaped particles. Therefore, if measuring the filler particle sizes by other techniques, slightly different values could be observed.

5           Thus, the carbonate polymer compositions included within the scope of this invention generally utilize such inorganic fillers with a number average particle size as measured by Coulter Counter of less than or equal to 10 micrometers ( $\mu\text{m}$ ) preferably less than or equal to 3  $\mu\text{m}$ , more preferably less than or equal to 2  $\mu\text{m}$ , more preferably less than or equal to 1.5  $\mu\text{m}$  and most preferably less than or equal to 1.0  $\mu\text{m}$ . Depending upon the grinding or  
10   preparation technique, such fillers can have number average particle sizes of at least 0.05  $\mu\text{m}$ , preferably at least 0.1  $\mu\text{m}$ , and more preferably at least 0.5  $\mu\text{m}$ . In general, the smaller average particle sizes, if available, could very suitably be employed but it has been found difficult to commercially obtain fillers of this type having an average particle size less than 1.5  $\mu\text{m}$ .

          In addition to having the specified small average particle size, it has also been  
15   found to be important in optimizing the filled blend impact properties to provide uniformly small particle-sized fillers where the number or amount of larger particles ("maximum particle size") is reduced. In this regard, preferred maximum particle size specifications have been determined for the most preferred fillers used in the blends according to the invention. Suitable fillers generally have a maximum particle size less than or equal to 50  $\mu\text{m}$ , preferably  
20   less than or equal to 30  $\mu\text{m}$ , more preferably less than or equal to 25  $\mu\text{m}$ , more preferably less than or equal to 20  $\mu\text{m}$  and most preferably less than or equal to 15  $\mu\text{m}$ .

          Another way of specifying the desired uniform small particle size and particle size distribution of the fillers preferably used in the practice of the present invention is to specify that at least 98 weight percent, preferably at least 99 weight percent, of the particles thereof in  
25   final blend have an equivalent spherical volume diameter less than 44  $\mu\text{m}$ , preferably less than 20  $\mu\text{m}$ . The weight percentage of the filler particles having such diameters can similarly be measured by particle size analysis with a Coulter Counter.

          In preparing the carbonate polymer compositions according to the present invention and obtaining optimized combinations of toughness, stiffness and resistance to  
30   thermal linear expansion, it has been found generally desirable to employ the inorganic filler(s) in an amount of at least 1, preferably at least 5 and more preferably at least 7 percent by weight based on weight of wax, filler, carbonate polymer, monovinylidene aromatic polymer and optional rubber. Usually it has been found sufficient to employ an amount of filler up to and including 20, preferably up to and including 17, more preferably up to and including 16  
35   percent by weight, which weight percentages are based on weights of wax, filler, carbonate polymer, monovinylidene aromatic polymer and optional rubber.

          With regard to obtaining optimized properties in articles prepared from the blend resins, it has been found that extremes in temperature conditions can result in poor



fitting of various components of the finished assembly unless the coefficient of linear thermal expansion (as measured according to ASTM D-696) is less than  $3.9 \times 10^{-5}/^{\circ}\text{F}$  ( $7 \times 10^{-5}/^{\circ}\text{C}$ ), preferably less than  $3.5 \times 10^{-5}/^{\circ}\text{F}$  ( $6.3 \times 10^{-5}/^{\circ}\text{C}$ ), and more preferably less than  $3.3 \times 10^{-5}/^{\circ}\text{F}$  ( $5.6 \times 10^{-5}/^{\circ}\text{C}$ ), over the temperature range of 70 to 120°F (21 to 49°C), preferably over the  
5 range of -22 to 185°F (-30 to 85°C).

It has surprisingly been found that injection molded components prepared from the resin blends of the present invention generally have an exceptionally smooth, defect-free, paintable surface finish. These features, together with the improved combinations of resistance to linear thermal expansion and low temperature toughness make these resins  
10 desirable for many applications such as injection molding, extrusion and blow molding of the resins into desirable shaped articles. In addition, extruded materials can be readily thermoformed into desired shaped articles.

The compositions according to the present invention are prepared by blending the foregoing components according to known blending and mixing techniques. Desirably the  
15 components may be first mixed or dry blended prior to melt blending in an appropriate extruder or other melt blending device. The components may be combined and blended in any order.

In addition to the foregoing components, additional additives may be included in the blend as long as they do not substantially deleteriously affect the other physical properties  
20 of the composition. Such additional additives may include, for example, pigments; light stabilizers such as U.V. absorbers; antioxidants; other processing aids such as lubricants and mold release agents; flame and dripping retardants; filler coupling agents, for example the polyfunctional organosilicon compounds disclosed in U.S. Patent 4,528,303 and other additives.

Having described the invention the following examples are provided as further  
25 illustrative and are not to be construed as limiting. Parts and percentages are based on weight.

As shown in the following tables, a series of filled polycarbonate/monovinylidene aromatic polymer blends were prepared varying the wax type, filler type, filler amount, carbonate polymer, monovinylidene aromatic polymer and rubber  
30 polymer component ratios. In addition to the components shown in the following tables, the blends also contained standard antioxidants and used epoxidized soybean oil to tackify the resin pellets to facilitate the combination of powdery additives such as the filler.

The carbonate polymer resins are commercially available grades of CALIBRE (TM) brand, bisphenol A-based polycarbonate (PC) produced by The Dow Chemical Company. The melt flow rates (MFR) are measured in grams per 10 minutes (g/10 min) according to ASTM  
35 D-1238, condition O while the weight average molecular weight values (Mw) are measured by gel permeation chromatography using a polystyrene standard.



Table 1

	MFR	M <sub>w</sub>	Trade Name
PC-7	7	30,700	CALIBRE* 300-7
PC-10	10	28,400	CALIBRE* 300-10
PC-13	13	26,800	CALIBRE* 300-13

5

The monovinylidene aromatic polymer resins are butadiene rubber modified copolymers of styrene ("STY") and acrylonitrile ("AN") commercially available as grades of MAGNUM (TM) brand, mass solution polymerized ABS produced by The Dow Chemical Company. As indicated below, the ABS components contain the indicated amounts of poly(styrene-acrylonitrile) ("SAN") as component (B) monovinylidene aromatic copolymer including amounts grafted to the rubber and butadiene rubber as optional rubber component (E), which butadiene rubber level does not include grafted SAN. The rubber levels are determined by the relative amounts of rubber and monomers incorporated during production of the ABS resin.

15

Table 2

	AN Concentration in SAN (wt %)	Rubber Level (wt %)	SAN Level (wt %)
ABS 1	18	12	88
ABS 2	29	20.5	79.5

20

In several of the compositions that were prepared an additional MBS grafted rubber impact modifier component was incorporated. This MBS was commercially available as Paraloid 8967 and according to the supplier's literature contains the below indicated levels of rubber and methylmethacrylate (MMA). The monovinylidene aromatic copolymer (MVAC) components are styrene, methyl methacrylate and small amounts of other crosslinking and proprietary comonomers and are substantially completely graft polymerized to the rubber.

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Table 3

	MMA Concentration in MVAC (wt %)	Rubber Level (wt %)	MVAC Level (wt %)
MBS	about 40	72	28

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The waxes and fillers that are used in the Experiments are summarized in the Tables below. The wax molecular weight (MW), Acid Number and Saponification Number values are reported from the supplier's literature.

Table 4

Wax Type	Trade Name	Density	MW	Acid Number	Saponification Number
Ester Wax (Montan derivative)	Hoechst Wachs E	1.01-1.03	about 780	15 - 20	130 - 160
Acid Wax (Montan derivative)	Hoechst Wachs S	1.00-1.02	about 580	130 - 150	155 - 175
Polar PE Wax	Hoechst Wachs PED 191	0.95-0.97	about 9,000	15 - 17	20 - 35
Non-Polar PE Wax	Hoechst Wachs PE 190	0.95-0.97	about 9,000	0	0
Bistearamide Wax	Hostalub FA1	0.99-1.01	about 780	< 15	< 15

The fillers used in the experiments were the commercially available mineral talcs identified below. Chemically these materials were hydrated magnesium silicates as represented by the formula:



For these fillers, their shape and ratio of the diameter to the thickness of the filler particles (D/T) were determined by preparing a filler modified polymeric resin sample, and preparing transmission electron photomicrographs (TEM's) of thin sections of the polymers at magnifications in the range of 3,000 to 15,000 X. Then shapes and sizes were determined by physically measuring the diameters and thicknesses for a representative sample of at least 25 filler particles and computing their ratio. The number average particle size and maximum particle size in micrometers ( $\mu\text{m}$ ) ("Ave. Particle Size" and "Max. Particle Size", respectively) are approximates ( $\pm 5\%$ ) and were determined by Coulter Counter analysis. The weight percentages of particles in the blend having a diameter less than  $20 \mu\text{m}$  ("Wt % <  $20 \mu\text{m}$ ") are also measured by Coulter Counter.

Table 5

Type	Trade Name	Shape	D/T	Ave. Particle Size ( $\mu\text{m}$ )	Max. Particle Size ( $\mu\text{m}$ )	Wt % < 20 $\mu\text{m}$
5 Talc	Microtalc MP 10-52	Plate	9.0	0.9	10	100
Talc	Microtalc MP 25-38	Plate	9.5	1.3	25	99

10 The components to be blended were dried for 4 hours at 210°F (99°C) in a circulated air dryer and then dry blended by tumble blending. The mixtures were then extruded under vacuum through a Werner Pfleiderer ZSK-30 twin screw extruder. The heaters were maintained at 518°F (270°C), the screw was run at 400 RPM, and the throughput rate was 30 lbs/hour (13.6 Kg/hr). Strands were cooled in a water bath and chopped. The granules were then dried for 4
   
 15 hours at 210°F (99°C) in a circulated air oven and molded into test specimens in an Arburg 28 ton injection molding machine at 550°F (288°C) melt temperature and 180°F (82°C) mold temperature.

The physical properties of the resulting injection molded samples were then measured and the test results are contained in the Tables below. The CLTE values, as measured by ASTM D-696 are given in units of "x 10<sup>-5</sup> millimeter per millimeter per degree Celsius" (x 10<sup>-5</sup>
  
 20 mm/mm °C) and "x 10<sup>-5</sup> inch per inch per degree Fahrenheit" (x 10<sup>-5</sup> in/in °F). Dart impact strength is measured according to ASTM D-3763-86 and is reported in inch-pounds (In-Lbs) and Joules (J). The Notched Izod values are determined according to ASTM D-256 and reported in foot pounds per inch (ft-lb/in) and Joules per meter (J/m).

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Table 6 - Effect of Different Waxes

	Control 1	Control 2	Ex. 1	Ex. 2	Ex. 3	Ex. 4
(A) PC-10	65	65	65	65	65	65
ABS 1	35	35	35	35	35	35
(B) SAN	30.8	30.8	30.8	30.8	30.8	30.8
(E) Rubber	4.2	4.2	4.2	4.2	4.2	4.2
(C) Bisteamide Wax	-	2.0	-	-	-	-
(C) Ester Wax	-	-	2.0	-	-	-
(C) Acid Wax	-	-	-	2.0	-	-
(C) Polar PE Wax	-	-	-	-	2.0	-
(C) Nonpolar PE Wax	-	-	-	-	-	2.0
(D) Talc MP10-52	13.0	13.0	13.0	13.0	13.0	13.0
Dart Impact						
73°F in-lbs Joules	372 42.0	189 21.4	384 43.4	370 41.8	351 39.7	334 37.7
-20°F in-lbs Joules	202 22.8	78 8.8	336 38.0	358 40.4	272 42.0	276 31.2
CLTE x 10-5 in/in °F x 10-5mm/mm °C	2.77 4.98	2.79 5.02	2.97 5.34	3.01 5.43	2.81 5.07	2.73 4.92
Notched Izod 73°F ft-lb/in J/m	7.6 406	1.4 75	8.9 475	6.2 331	10.1 539	8.3 443
Notched Izod -20°F ft-lb/in J/m	2.4 128	1.4 75	2.8 149	2.3 123	2.9 155	2.5 133

Table 7 - Effect of Talc Particle Size

	Control 3	Ex. 5	Control 4	Ex. 6
(A) PC-10	65	65	65	65
5 ABS 1	35	35	35	35
(B) SAN	30.8	30.8	30.8	30.8
(E) Rubber	4.2	4.2	4.2	4.2
(C) Ester Wax	-	2.0	-	2.0
(D) Talc MP10-52	14.0	14.0	-	-
10 (D) Talc MP25-38	-	-	14.0	14.0
Dart Impact				
73°F in-lbs	320	300	286	279
Joules	36.2	33.4	32.3	31.5
-20°F in-lbs	276	315	97	127
15 Joules	31.2	35.6	11.0	14.3
CLTE				
x 10 <sup>-5</sup> in/in °F	2.72	2.89	2.86	3.05
x 10 <sup>-5</sup> mm/mm °C	4.90	5.20	5.14	5.49
Notched Izod 73°F				
ft-lb/in	7.2	8.4	3.8	5.3
20 J/m	384	448	203	282
Notched Izod -20°F				
ft-lb/in	1.8	2.3	1.6	1.7
J/m	96	123	101	91

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Table 8

	Control 5	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
(A) PC-7						63.4	-
(A) PC-13						-	63.4
(A) PC-10	65	65	61.8	63.4	63.4		
ABS 1	35	35	33.3	34.2	34.2	34.2	34.2
(B) SAN	30.8	30.8	29.3	30.1	30.1	30.1	30.1
(E) Rubber	4.2	4.2	4.0	4.1	4.1	4.1	4.1
MBS	-	-	4.9	2.4	2.4	2.4	2.4
(B) S-MMA			1.4	0.7	0.7	0.7	0.7
(E) Rubber			3.5	1.7	1.7	1.7	1.7
(C) Ester Wax	-	2.0	2.0	2.0	2.0	2.0	2.0
(D) Talc MP 10-52	14.5	14.5	14.5	13.0	16.0	14.5	14.5
Dart Impact							
73°F in-lbs	352	350	361	380	370	352	368
Joules	39.8	39.5	40.8	42.9	41.8	39.8	41.6
-20°F in-lbs	99	306	296	340	231	326	300
Joules	11.2	34.6	33.4	38.4	26.1	36.8	33.9
CLTE x 10 <sup>-5</sup> in/in °F				3.1	3.2		
x 10 <sup>-5</sup> mm/mm °C				5.6	5.8		
Notched Izod 73°F							
ft-lb/in	3.0	7.1	7.7	8.5	6.4	8.2	6.9
J/m	160	379	411	454	391	438	368
Notched Izod -20°F							
ft-lb/in	-	-	-	-	1.6	2.0	1.8
J/m	-	-	-	-	85	107	96

Table 9

	Ex. 13	Ex. 14	Ex. 15	Ex. 16
(A) PC-10	58.6	68.4	65	65
5 ABS 1	39.0	29.2	35	-
(B) SAN	34.3	25.7	30.8	-
(E) Rubber	4.7	3.5	4.2	-
ABS 2			-	35.0
(B) SAN				27.8
(E) Rubber				7.2
10 MBS	2.4	2.4		
(B) S-MMA	0.7	0.7		
(E) Rubber	1.7	1.7		
PC/ABS Ratio	1.50	2.33	1.86	1.86
(C) Ester Wax	2.0	2.0	2.0	2.0
(D) Talc MP10-52	14.5	14.5	14.0	14.0
15 Dart Impact				
73°F in-lbs	355	376	300	300
Joules	40.1	42.5	33.9	33.9
-20°F in-lbs	305	290	315	288
Joules	34.5	32.8	35.6	32.5
20 CLTE				
x 10 <sup>-5</sup> in/in °F				
x 10 <sup>-5</sup> mm/mm °C			2.89	2.80
			5.20	5.05
Notched Izod 73°F				
ft-lb/in.	6.8	8.5	8.4	6.6
J/m	363	454	448	352
25 Notched Izod -20°F				
ft-lb/in	1.6	2.1	2.3	1.7
J/m	85	112	123	91

30 As can be seen, the selection of the wax additive and the inorganic filler provide the claimed blends with surprising combinations of properties that are not attainable when the proper wax additive or the proper filler type are not employed.

Experimental compositions 17 and 18 were prepared in accordance with Experiments 1 and 9 above but containing 1 percent of the ester wax instead of 2 percent as in Experiments 1 and 9.

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Table 10

	Ex. 17	Ex. 18
(A) PC-10	51.4	53.7
5 ABS 1 (B) SAN (E) Rubber	27.7	28.9
MBS (B) S-MMA (E) Rubber		2.0
10 (C) Ester Wax	1.0	1.0
(D) Talc MP 10-52	13	13

These compositions were injection molded into plaques and exterior automotive door panels. Both materials had a 10 percent improvement in processability, as measured by injection pressure and capillary rheology, over the same materials without wax. The plaques were painted and subjected to Distinctness of Reflected Image Gloss (ASTM-E-430-83), 20 Degree Specular Gloss (ASTM D-523-85), Tape Adhesion Test for Paint Finishes (General Motors Test GM9071P), Knife Cross-Hatch Adhesion (General Motors Test GM9502P), Humidity Aging (General Motors Test GM4465P), and Chip Resistance of Coating (General Motors Test BM9508P) testing. The material passed all of these tests. The body panels were painted and passed one year durability testing.

1. A filled polymer blend composition comprising (A) carbonate polymer; (B) monovinylidene aromatic copolymer; (C) an effective amount of a wax which improves the low temperature toughness of the blend; (D) a plate-shaped inorganic filler which has a number average particle size less than or equal to 10 micrometers ( $\mu\text{m}$ ) and an average diameter to thickness ratio (D/T) of from 4 to 30; and optionally (E) a rubber impact modifier.
2. A filled polymeric blend composition according to Claim 1 comprising (A) carbonate polymer in an amount of from 50 to 95 percent by weight based on weight of components (A), (B) and (E); (B) monovinylidene aromatic copolymer in an amount of from 5 to 50 percent by weight based on weight of components (A), (B) and (E); (C) a wax in an amount of from 0.1 to 5 percent by weight based on weight of components (A), (B), (C), (D) and (E); and (D) an inorganic filler in an amount of from 1 to 17 percent by weight based on weight of components (A), (B), (C), (D) and (E); and (E) a rubber impact modifier in an amount of from 1 to 20 percent by weight based on weight of components (A), (B) and (E).
3. A filled polymeric blend composition according to Claim 1 wherein the wax additive is selected from the group consisting of ester waxes, polyethylene waxes, acid waxes and blends of two or more of these waxes.
4. A filled polymeric blend composition according to Claim 1 wherein the wax additive comprises ester wax.
5. A filled polymeric blend composition according to Claim 1 wherein the inorganic filler is selected from the group consisting of talc and clay.
6. A filled polymeric blend composition according to Claim 1 wherein the filler has an average diameter/thickness ratio of from 6 to 30.
7. A filled polymeric blend composition according to Claim 1 wherein the filler has an average diameter/thickness ratio of from 9 to 20.
8. A filled polymeric blend composition according to Claim 1 wherein at least 99 percent of the filler has a particle diameter less than 20  $\mu\text{m}$ .
9. A filled polymeric blend composition according to Claim 1 wherein the inorganic filler is a hydrated magnesium silicate talc.
10. A composition according to Claim 9 wherein the talc has a composition as generally represented by the formula:  $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ .
11. A composition according to Claim 1 wherein the inorganic filler has an average particle size of 2  $\mu\text{m}$  or below.
12. A composition according to Claim 1 wherein the inorganic filler has an average particle size of 1.5  $\mu\text{m}$  or below.
13. A composition according to Claim 1 wherein the inorganic filler has a maximum particle size of 30  $\mu\text{m}$  or below.
14. A composition according to Claim 1 wherein the inorganic filler has a maximum particle size of 25  $\mu\text{m}$  or below.

15. A composition according to Claim 1 wherein the carbonate polymer comprises in polymerized form one or more dihydroxy monomers selected from the group consisting of bisphenol A, tetrabromo-bisphenol A, tetramethyl bisphenol A, 1,1-bis(4-hydroxyphenyl)-1phenylethane, or bishydroxyphenylfluorene.

5 16. A composition according to Claim 15 wherein the carbonate polymer consists of bisphenol A as the dihydroxy monomer.

17. A composition according to Claim 1 wherein the carbonate polymer has a melt flow rate from 3 to 80.

10 18. A composition according to Claim 1 wherein the carbonate polymer has a melt flow rate from 6 to 30.

19. A polymeric blend according to Claim 1 comprising a monovinylidene aromatic copolymer (B) comprising copolymerized therein styrene and acrylonitrile and a grafted rubber impact modifier component (E) which is a homopolymer or copolymer of butadiene or an interpolymer of ethylene, propylene and a nonconjugated diene.

15 20. A molded article prepared from a composition according to Claim 1.

21. A molded article according to Claim 20 which is an exterior automobile body panel.

22. A molded article according to Claim 20 having a surface area greater than 400 square inches, which article has a coefficient of linear thermal expansion (CLTE) equal to or  
20 less than  $3.7 \times 10^{-5}/^{\circ}\text{F}$  ( $6.7 \times 10^{-5}/^{\circ}\text{C}$ ).

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/09907

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L69/00 C08K3/34 C08K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 391 413 (THE DOW CHEMICAL CO.) 10 October 1990 cited in the application see claims 1,5-7 ---	1-8, 11-16
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-357309(45) & JP,A,5 262 955 (JAPAN SYNTHETIC RUBBER CO. LTD.) 12 October 1993 see abstract ---	1-8, 11-16
A	EP,A,0 452 788 (GE PLASTICS) 23 October 1991 see claim 1 --- -/-	1-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \* "P" document published prior to the international filing date but later than the priority date claimed

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- \* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- \* "&" document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/09907

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 219 936 (HONKOMP D.J. ET AL) 15 June 1993 see claim 1; examples 1-8 ---	1-16
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 84-215852(35) & JP,A,59 124 999 (DAINICHISEIKA COLOR CHEM) 19 July 1984 see abstract ---	1,3,4
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/09907

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